Thermochemistry of CaO-MgO-Al_2O_3-SiO_2 (CMAS) and Advanced Thermal and Environmental Barrier Coating Systems

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Outline of Presentation

- Thermal and Environmental Barrier Coating Systems
- Experimental

- Sample preparation and reaction with CMAS
- Results

- Thermodynamic modeling of YSZ-CMAS system

- Characterization:

1 - Pristine NASA composition CMAS by XRD, ICP-OAS and DSC

2 - CMAS reacted with the hollow tube coating specimens by SEM-EDS and XRD

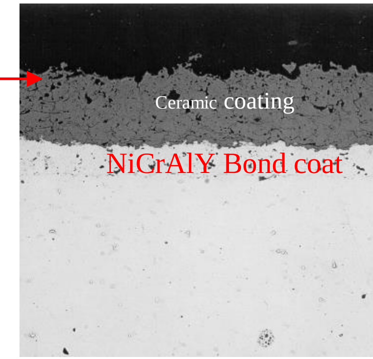
- Summary

Thermal and Environment Barrier Coating Developments

Baseline ZrO_2-(7-8)wt%Y_2O_3 and Rare Earth Doped-Low Conductivity Thermal Barrier Coating Systems - Continued

Baseline ZrO_2-(7-8) wt%Y_2O_3:

- Relatively low intrinsic thermal conductivity ~2.5 W/m-K
- High thermal expansion to better match superalloy substrates
- Good high temperature stability and mechanical properties
- Additional conductivity reduction by micro-porosity



Low Conductivity Defect Cluster Thermal Barrier Coatings

— Multi-component oxide defect clustering approach

e.g.: ZrO_2/HfO_2-Y_2O_3-Nd_2O_3(Gd_2O_3,Sm_2O_3)-Yb_2O_3(Sc_2O_3) systems

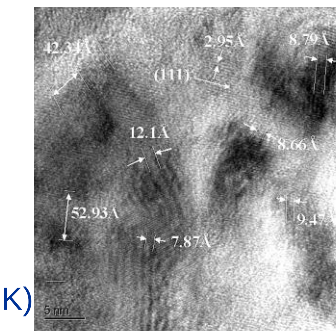
Primary stabilizer

Oxide cluster dopants with distinctive ionic sizes

— Defect clusters associated with dopant segregation

— The 5 to 100 nm size defect clusters for significantly reduced thermal conductivity (0.5-1.2 W/m-K) and improved stability

— Advanced TEBC systems for Ceramic Matrix Composites use the low k based compositions

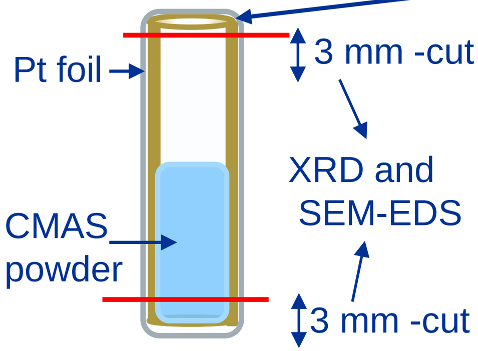


Plasma-sprayed ZrO_2-(Y, Nd,Yb)$_2O_3$

TEBCs-CMAS Degradation is of Concern with Increasing Operating Temperatures

Experimental:sample preparation and heat treatment

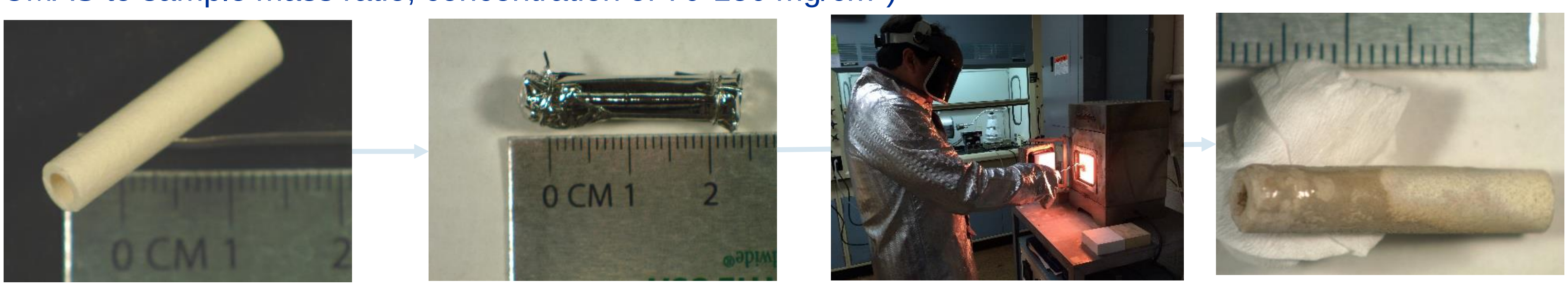
- Air plasma sprayed coating (0.030” thickness) specimens on to 1/8” diameter graphite bar substrates then 1500 °C, 5 h sintering, resulting hollow tubes.
- NASA composition CMAS used for reaction at 1300 ° C for 5h.



	Hollow Tube composition mole (%)	ρ (%) *	Average pore vol. (mm^3) **
cubic	ZrO_2-$12Y_2O_3$	90(3)	35(2)
	ZrO_2- $18Y_2O_3$	81(3)	-
	HfO_2-$7Dy_2O_3$	89(3)	21(3)
	ZrO_2- $9Y_2O_3$- $4.5Gd_2O_3$- $4.5Yb_2O_3$	100 (3)	3(7)
	ZrO_2- $9.6Y_2O_3$- $2.2Gd_2O_3$- $2.1Yb_2O_3$	90(3)	23(4)
tetragonal	ZrO_2- $3Y_2O_3$- $1.5Nd_2O_3$- $1.5Yb_2O_3$- $0.3Sc_2O_3$	90(3)	20(3)
	ZrO_2- $3Y_2O_3$-$1.5Sm_2O_3$-$1.5Yb_2O_3$	98(3)	4(3)

*(ρgeometric*100/ρHe). **ρgeometric-ρHe.

(1:10 CMAS to sample mass ratio, concentration of 70-150 mg/cm^2)



(A) (B) (C)

Hollow 12YSZ tube samples: (A) pristine; (B) before heat treatment in which it was half filled with CMAS powder, wrapped and sealed with Pt foil; (C) after heat treatment at 1310 °C for 30 min and unwrapped.

Results: characterization of NASA composition CMAS (as processed) before reaction

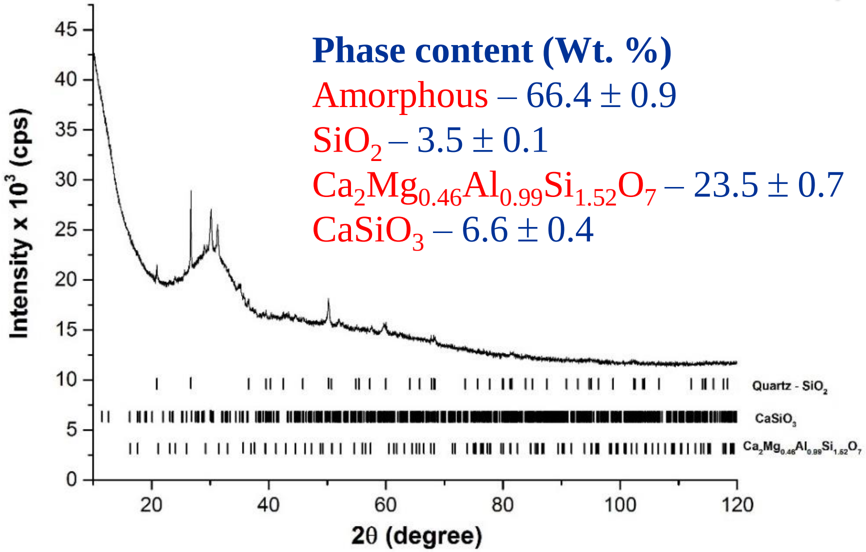
Phase content (Wt. %)

Amorphous – 66.4 ± 0.9

SiO_2 – 3.5 ± 0.1

$Ca_2Mg_{0.46}Al_{0.99}Si_{1.52}O_7$ – 23.5 ± 0.7

$CaSiO_3$ – 6.6 ± 0.4

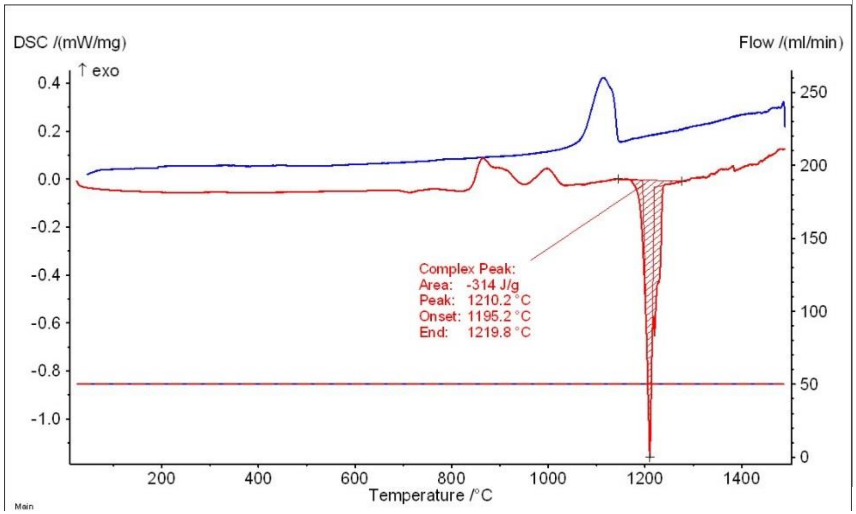


X-ray diffraction patterns of the as-received CMAS sample.

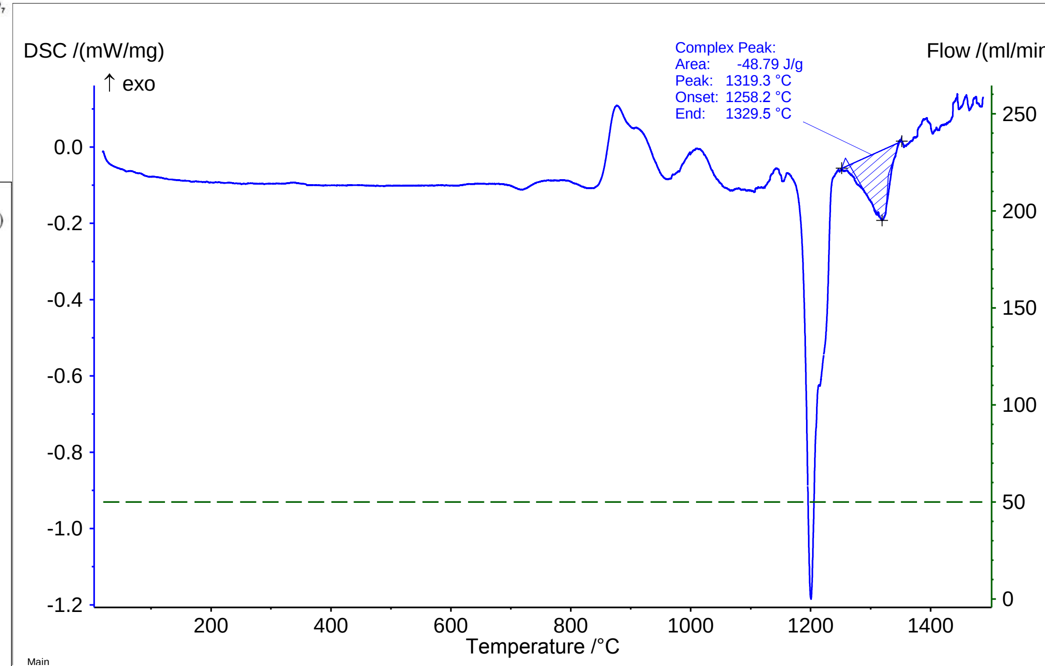
Chemical analysis of the as-received NASA CMAS by ICP-OAS

Element	Amount (wt. %)	±
Ca	21	1
Mg	3.1	0.2
Al	6.1	0.3
Si	19	1
Fe	5.9	0.3
Ni	1.10	0.06

Trace elements found but not quantified are Ba, Cr, Cu, K, Mn, Na, Sr, Ti, Zr



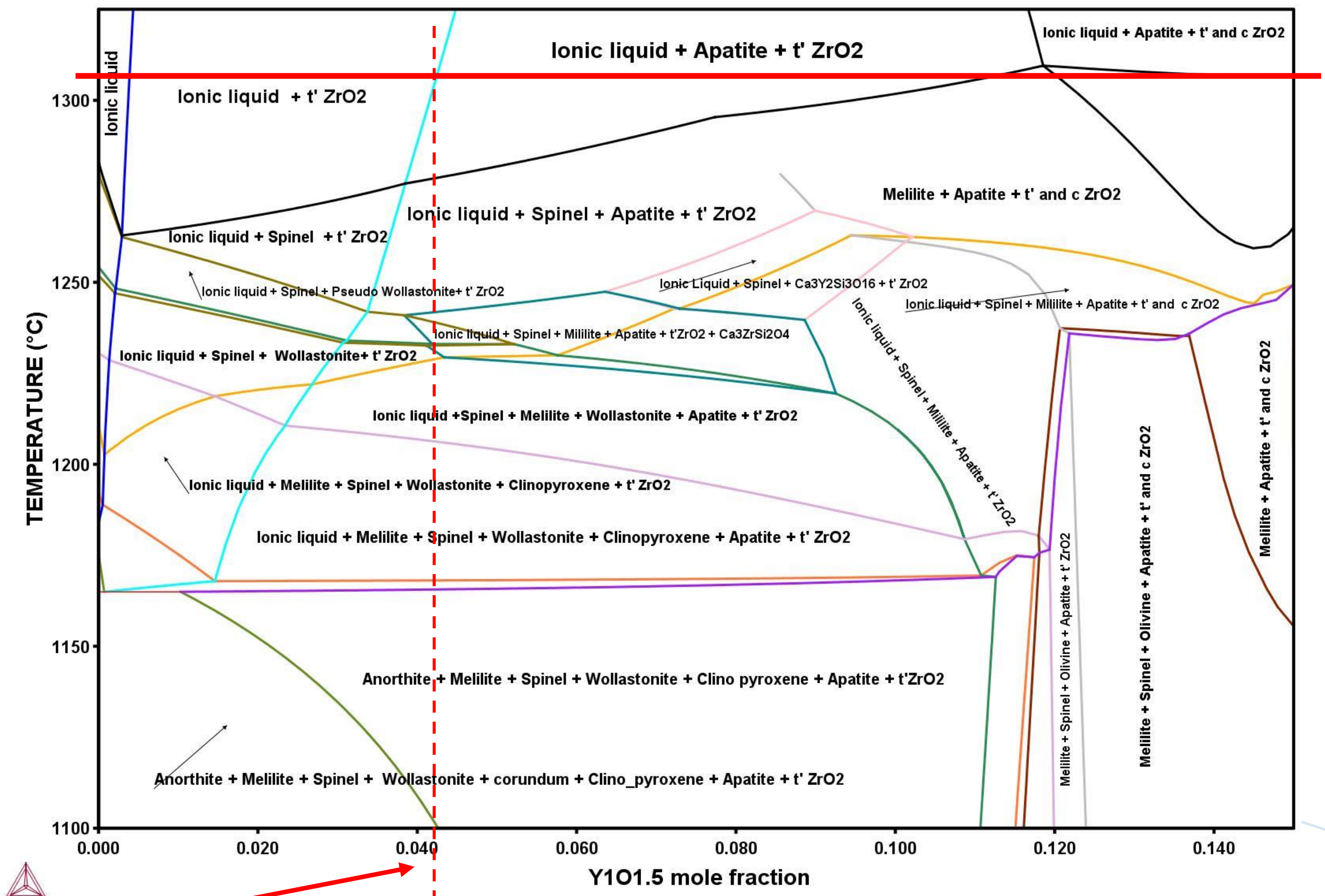
DSC traces of CMAS during heating and cooling up to 1500 °C at 5 °C/min.



DSC traces of CMAS mixed with 18YSZ (1:2 mass ratio) during **heating** up to 1500 °C at 5 °C/min.

Results: Thermochemical modeling of YSZ – CMAS system using Thermocalc and TCOX6 database

2017.01.19.16.35.05
TCOX6: ALO1.5, CAO, MGO, SIO2, Y1O1.5, ZRO2, NIO, FEO1.5, O
P=1.01325E5, N=1., 35*X(MGO)-8*X(CAO)=1.97196E-11, 8*X(ALO1.5)-7*X(MGO)=-6.67894E-12, 45*X(ALO1.5)-7*X(SIO2)=-3.62195E-11, 45*X(FEO1.5)-7*X(SIO2)=3.35021E-12, 3*X(NIO)-X(FEO1.5)=-2.72796E-13, 82*X(Y1O1.5)-18*X(ZRO2)=-2.43361E-13, ACR(O)=1



Reaction T of the experiments

Calculated phase diagram of CMS-YSZ system.

Input oxide amounts

Component	Mole
CaO	35
MgO	8
Al_2O_3	7
SiO_2	45
Fe_2O_3	3
NiO	1
ZrO_2	82
Y_2O_3	18

8 mol% Y_2O_3

2.3 mol% Y_2O_3
Baseline TBC

Output:
T - 1316.85 °C

Fluoride

Component	Mol
CaO	1.7e-2
MgO	2.5e-3
$FeO_{1.5}$	1.7e-7
$AlO_{1.5}$	1e-3
NiO	4.4e-3
SiO_2	3.0e-5
ZrO_2	8.9e-1
$Y_1O_{1.5}$	8.4e-2

ZrO2_tetragonal

Component	Mol
CaO	8.1e-3
MgO	5.1e-5
$FeO_{1.5}$	8.6e-8
NiO	3.8e-3
ZrO_2	9.7e-1
$Y_1O_{1.5}$	1.8e-2

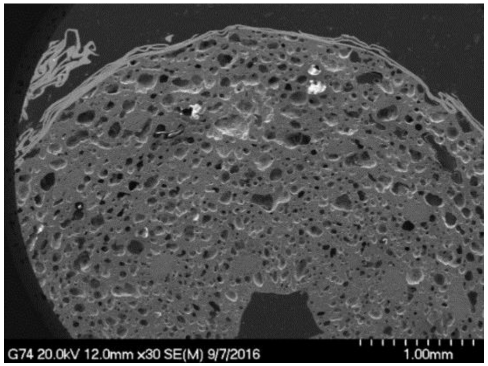
Apatite

Component	Mol
CaO	1.1e-1
MgO	2e-4
SiO_2	2.7e-1
$Y_1O_{1.5}$	6.2 e-1

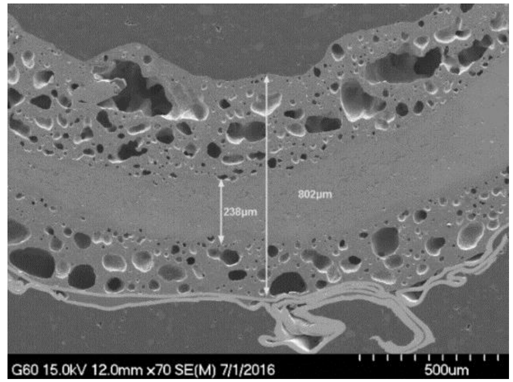
Ionic_liq#2

Component	Mol
CaO	2.8e-1
MgO	9.3e-2
SiO_2	3.8e-1
$FeO_{1.5}$	9.3-1
NiO	2.2e-2
ZrO_2	2.7e-2

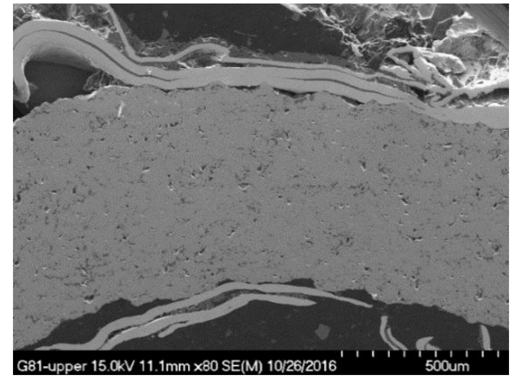
Results: SEM cross-section images at low magnification (lower cut section)



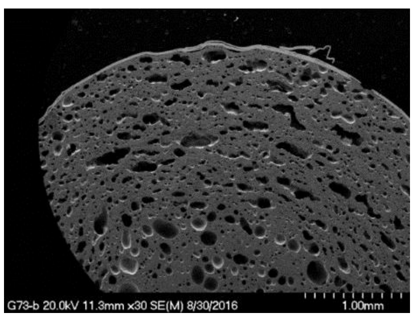
12YSZ



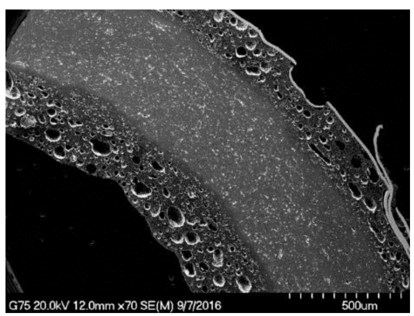
18YSZ



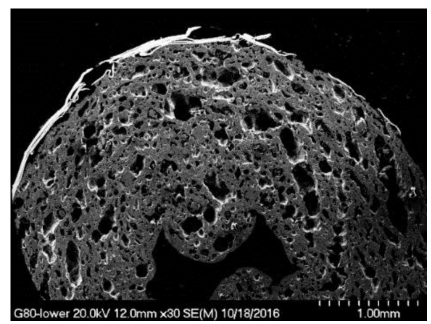
7DySH



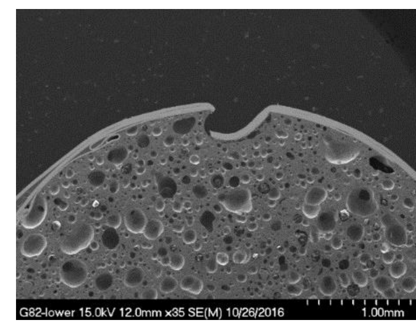
ZrO_2-9.0Y_2O_3-4.5Gd_2O_3-4.5Yb_2O_3



ZrO_2-9.6Y_2O_3-2.2Gd_2O_3-2.1Yb_2O_3



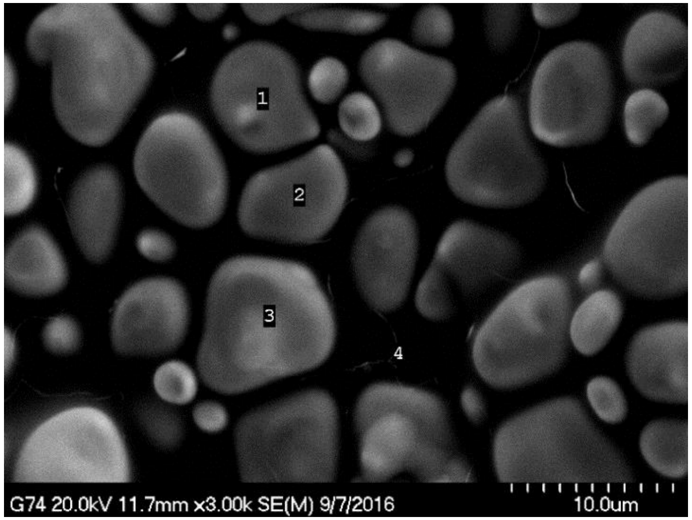
ZrO_2-3.0Y_2O_3-1.5Sm_2O_3-1.5Yb_2O_3



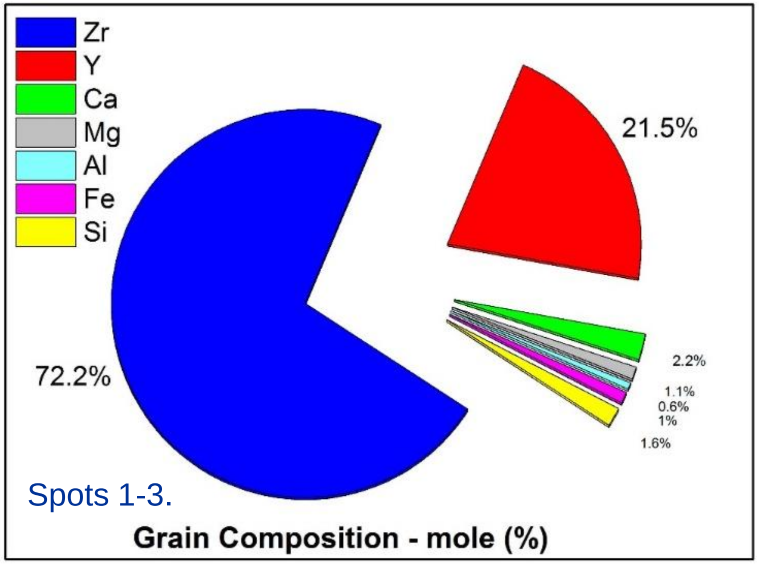
ZrO_2-3.0Y_2O_3-1.5Nd_2O_3-1.5Yb_2O_3-0.3Sc_2O_3

SEM cross – sectional electron images of the lower section of the ceramic hollow tube samples reacted with CMAS at 1300 °C for 5 h.

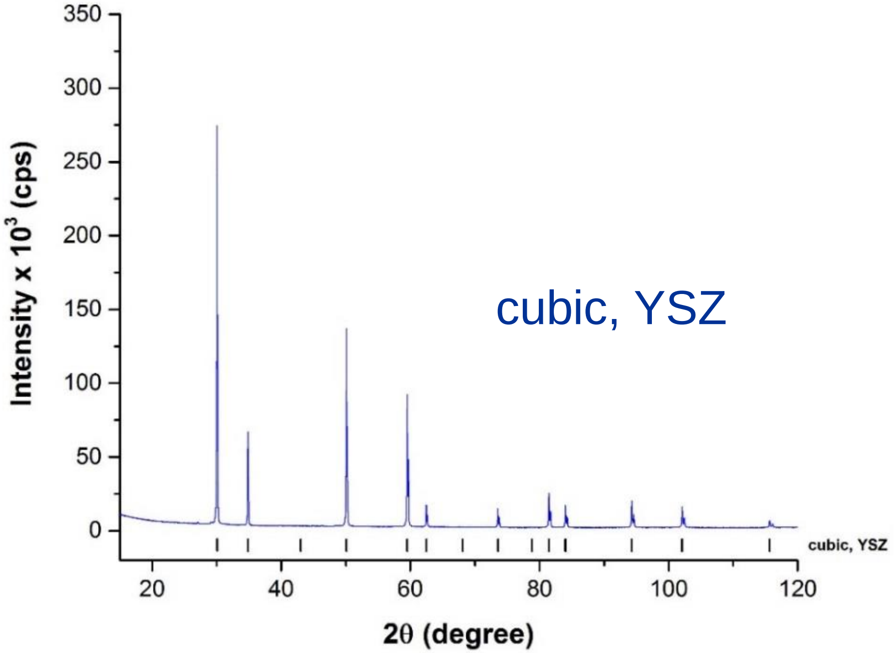
Results: 12YSZ lower section of the hollow tube reacted with CMAS.



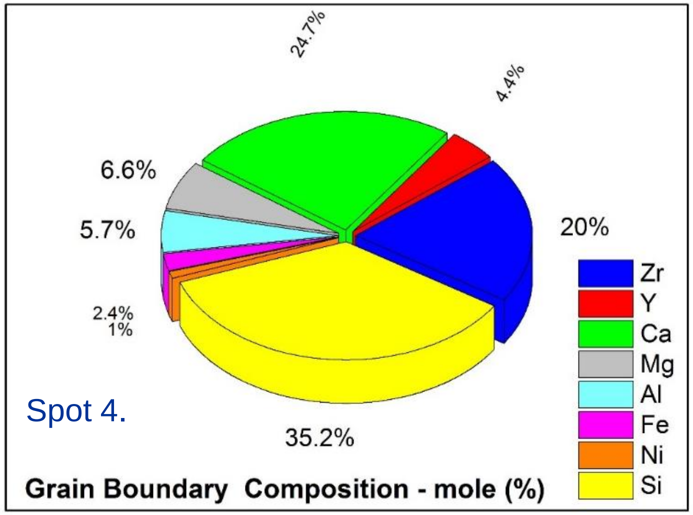
SEM image of (reacted region) at high magnification.



Grains 1-3	ZrO_2	Y_2O_3
Nominal mole (%)	88	12
EDS mole (%)	81 (1)	11.9(2)

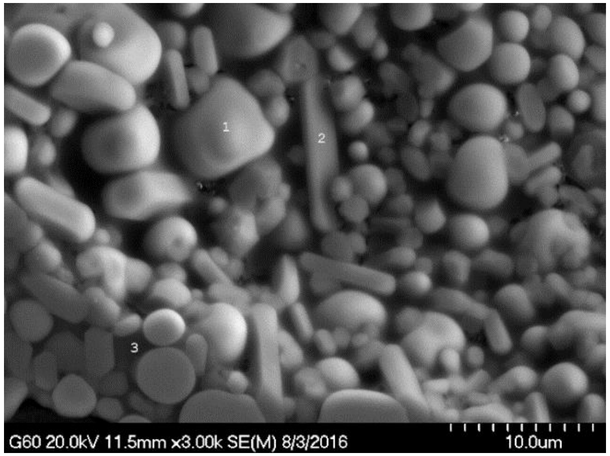


XRD pattern of the ground hollow tube.

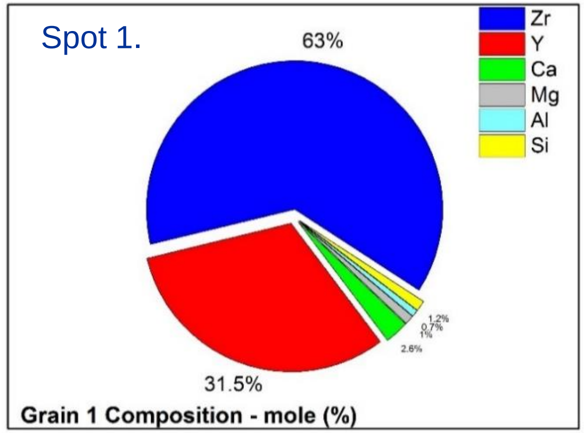


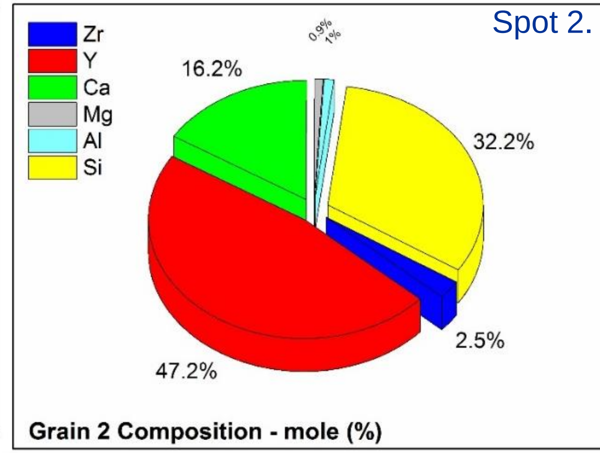
Elemental content from EDS.

Results: 18YSZ lower section of the hollow tube reacted with CMAS.

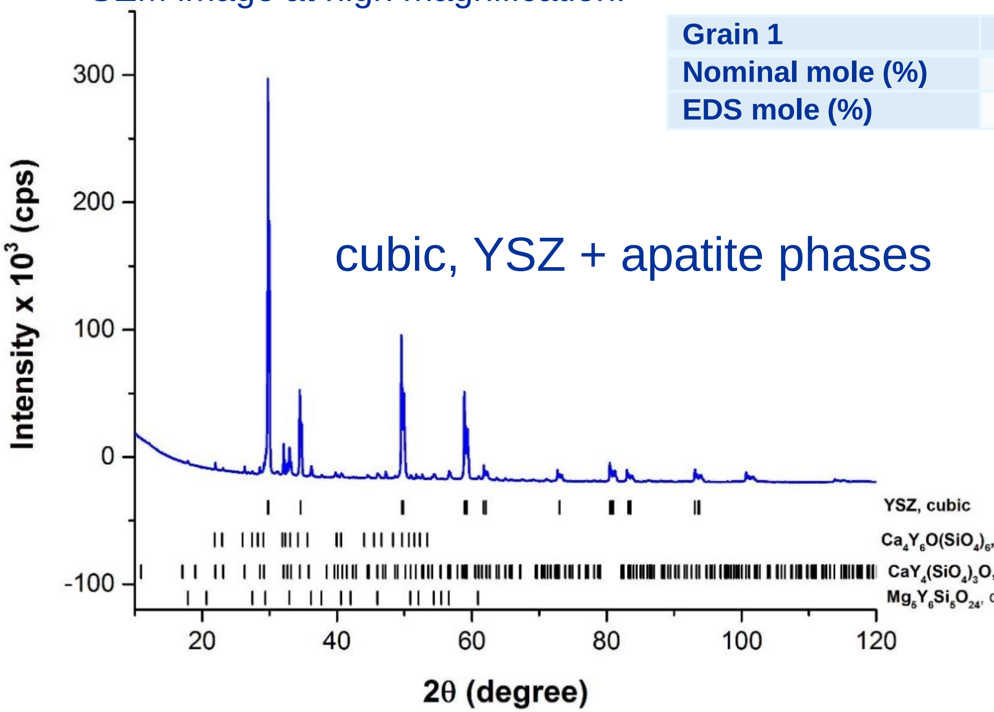


SEM image at high magnification.

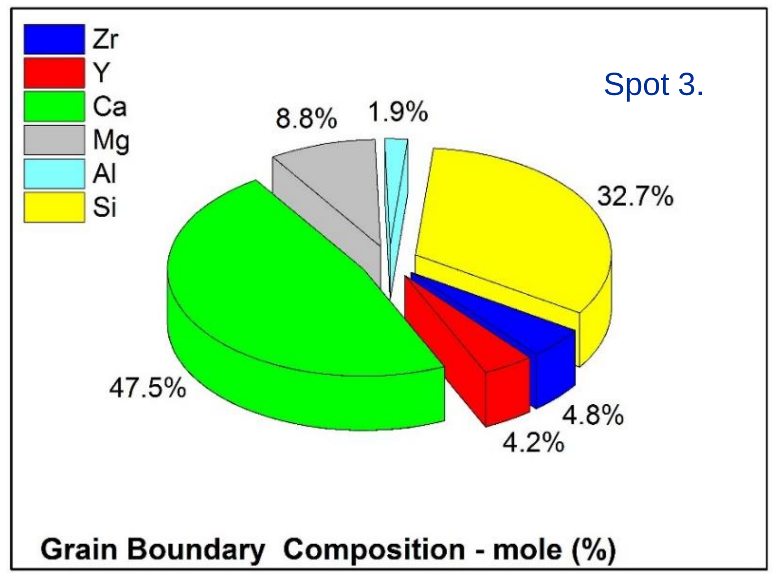




Grain 1	ZrO_2	Y_2O_3
Nominal mole (%)	81	18
EDS mole (%)	75(2)	19(1)

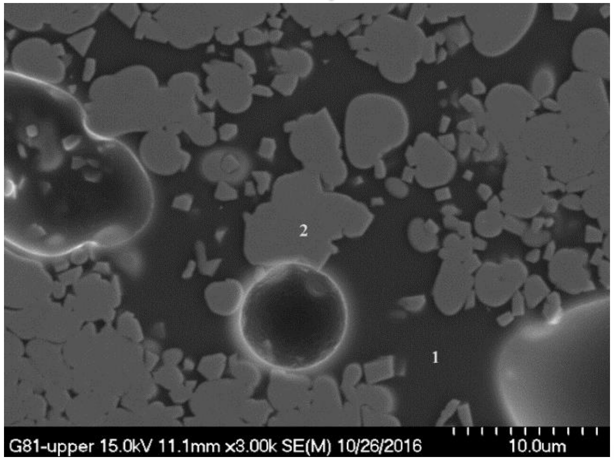


X-ray diffraction of the ground hollow tube.

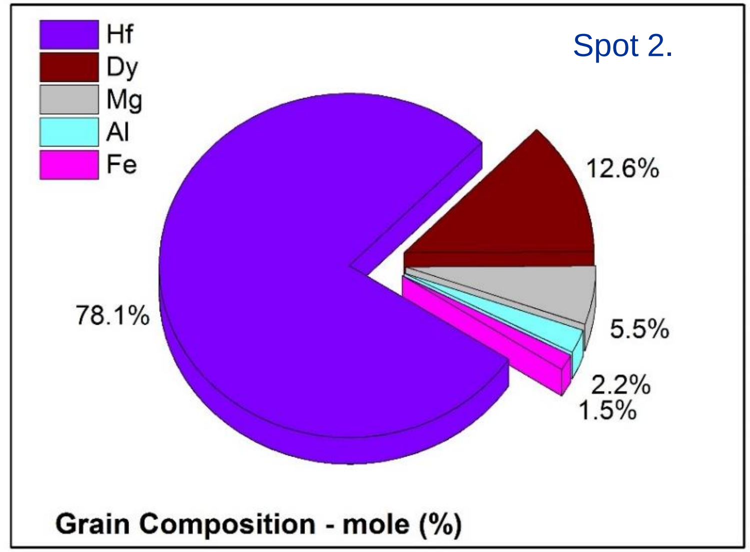


Elemental content from EDS.

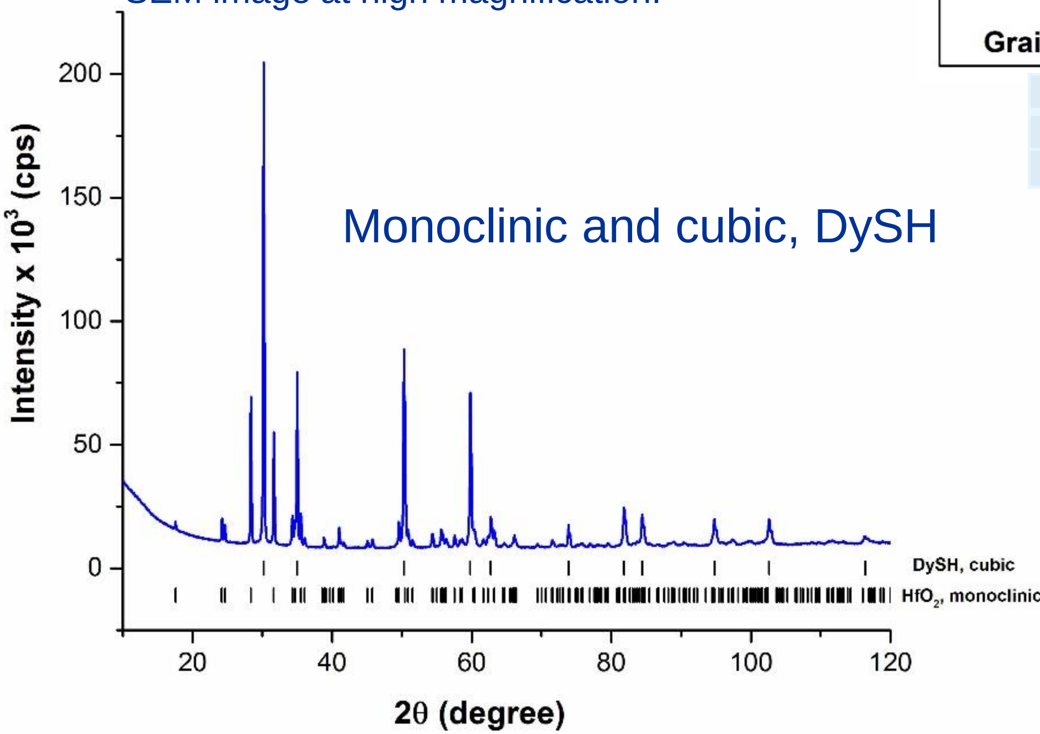
Results: 7DySH lower section of the hollow tube reacted with CMAS.



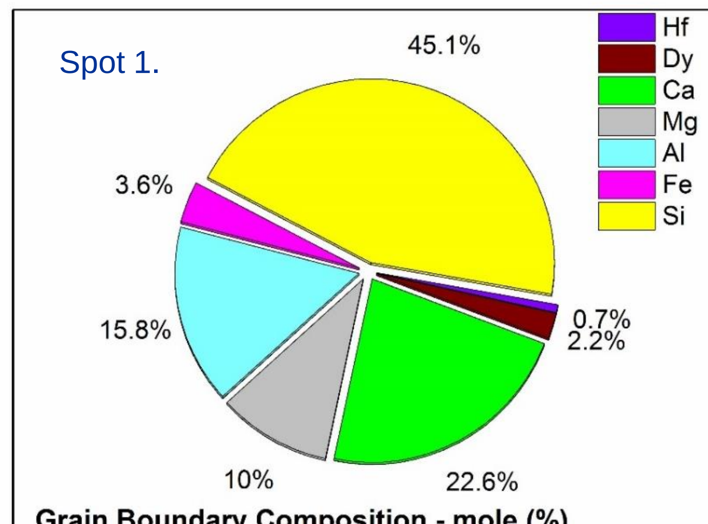
SEM image at high magnification.



Grain 2	HfO_2	Dy_2O_3
Nominal mole (%)	93	7
EDS mole (%)	85(5)	7(1)

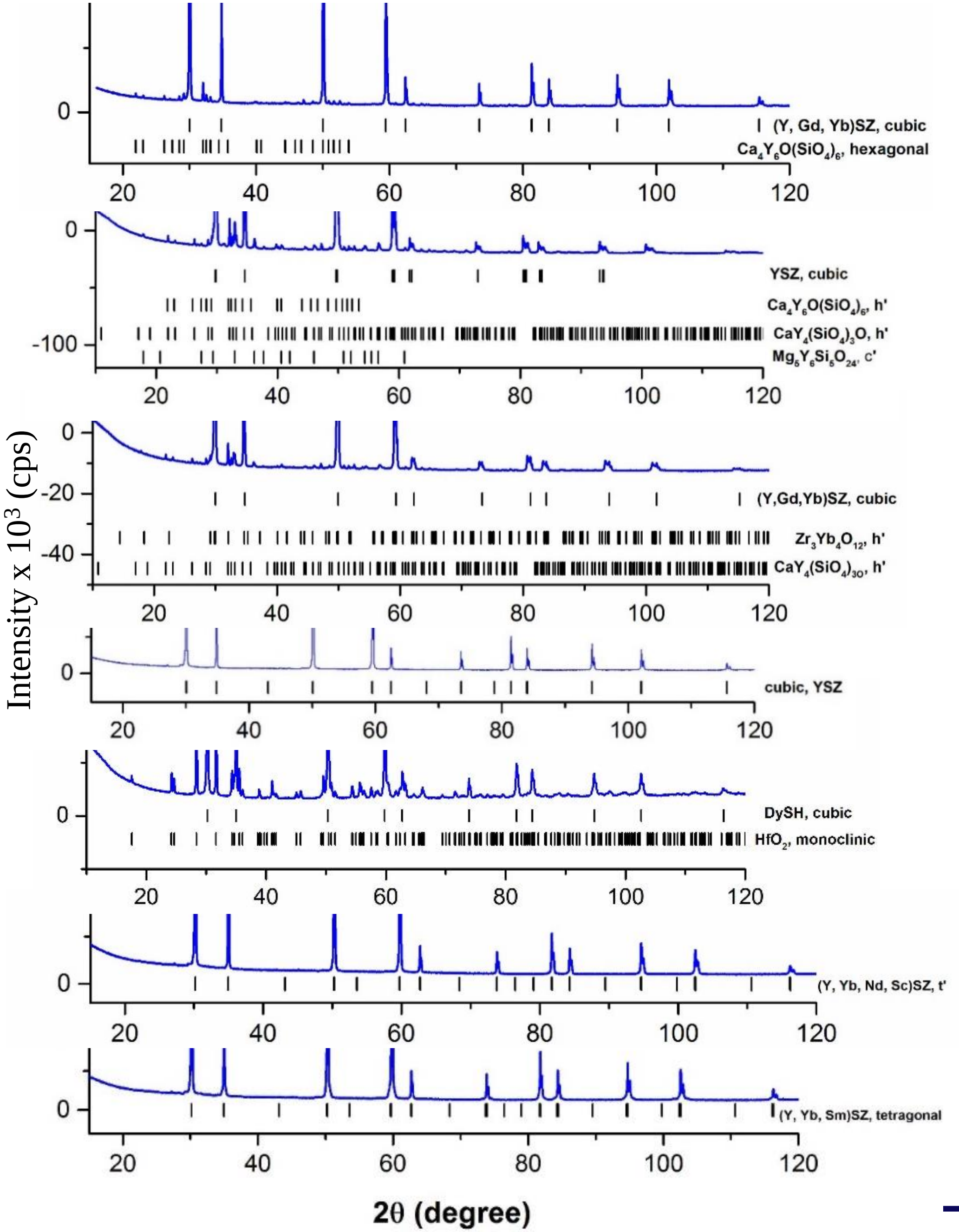


XRD pattern of the ground hollow tube.



Elemental content from EDS.

Results Rare Earth Content *versus* apatite phase formation.



ZrO_2-18RE_2O_3 (RE = Y, Gd and Yb)

ZrO_2-18Y_2O_3

ZrO_2-13.9RE_2O_3 (RE = Y, Gd and Yb)

ZrO_2-12Y_2O_3

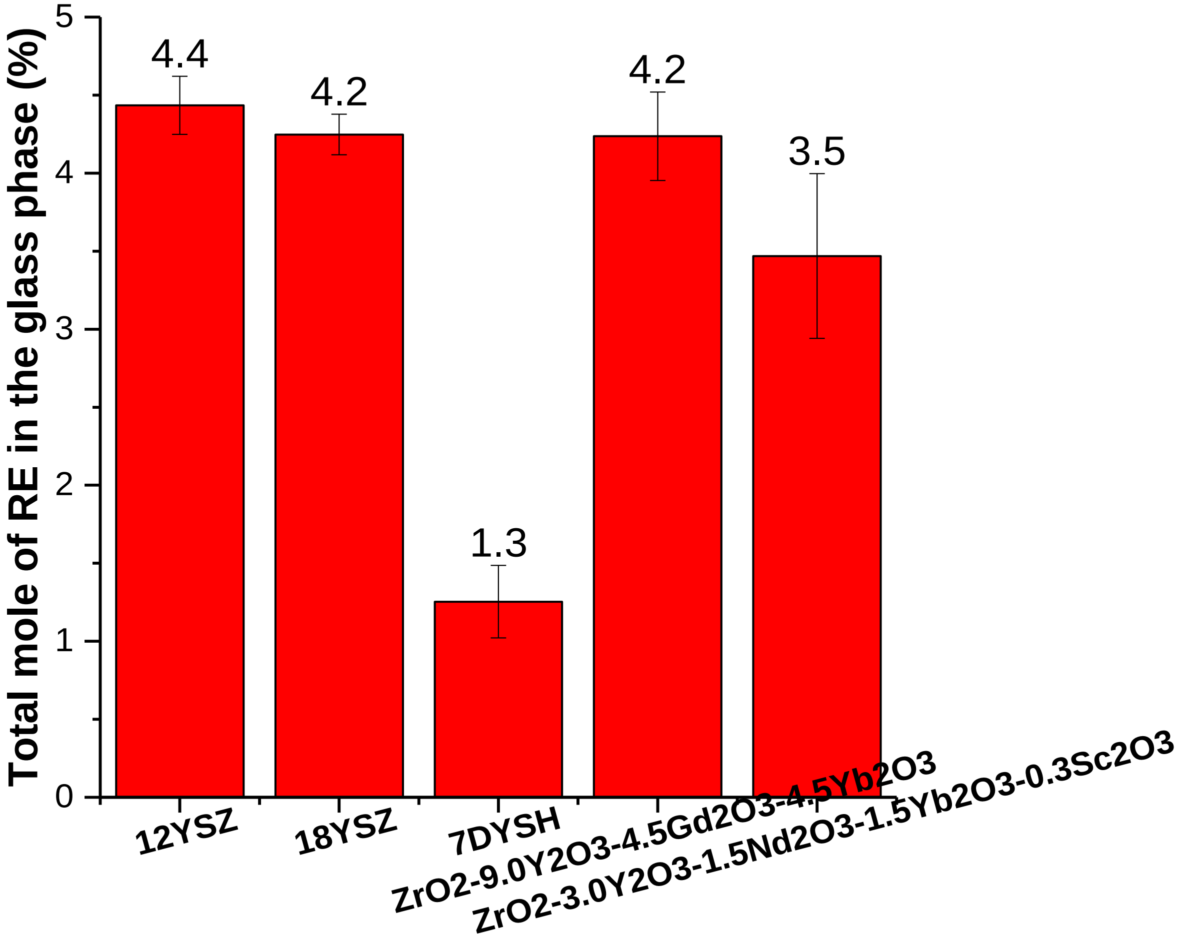
HfO_2-6.3Dy_2O_3

ZrO_2-6.3RE_2O_3 (RE = Y, Nd, Yb and Sc)

ZrO_2-6.0RE_2O_3 (RE = Y, Sm and Yb)

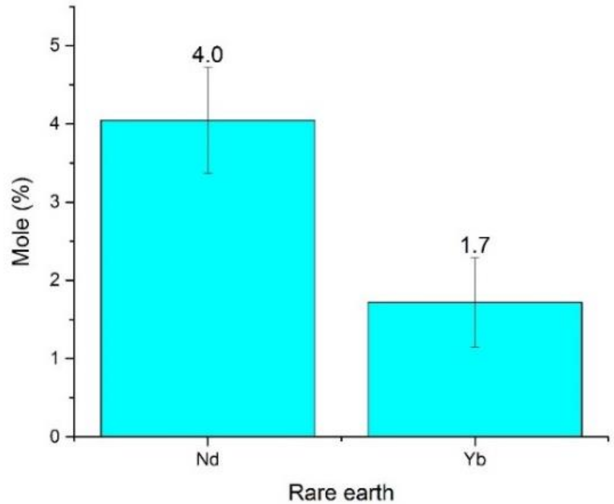
XRD patterns of the ground hollow tubes reacted with CMAS at 1310 °C for 5 h (lower cut section).

Results: content of the Rare-earth in the glass/silicate phase.

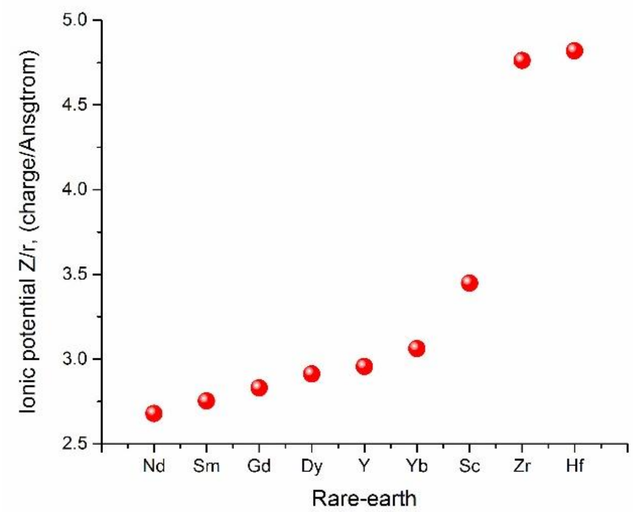


Depedence of the Rare-earth content in the glass/silicate phase versus Rare-earth content in the coating.

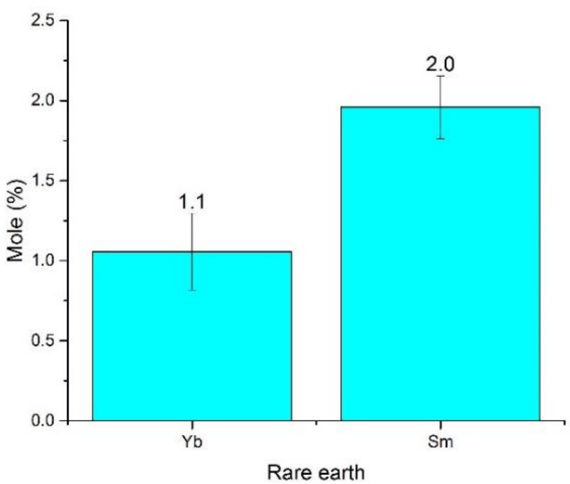
Results: content of the Rare-earth in the glass/silicate phase.



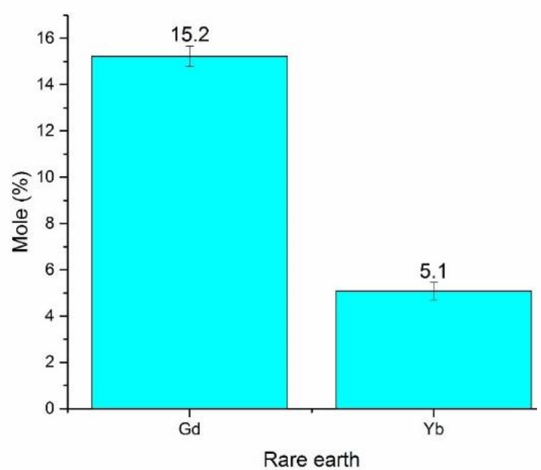
ZrO_2-3.0Y_2O_3-1.5Nd_2O_3-1.5Yb_2O_3-0.3Sc_2O_3



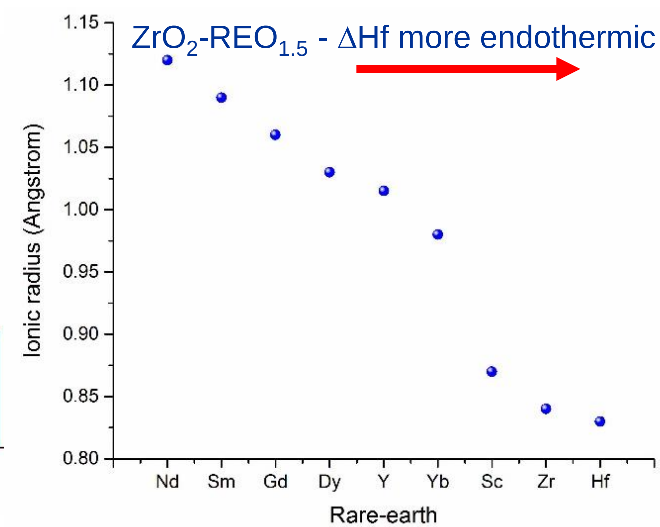
Ionic potential trend of RE



ZrO_2-3.0Y_2O_3-1.5Sm_2O_3-1.5Yb_2O_3



ZrO_2-9.6Y_2O_3-2.2Gd_2O_3-2.1Yb_2O_3



Radius size trend of RE

Summary

- Thermochemical reactions between CMAS and EBC and TBC materials were studied at 1310 °C for 5h.
- CMAS penetrated the samples at the grain boundaries and dissolved the EBC/TBC material to form silicate glassy and orthosilicate crystalline phases containing the rare-earth elements.
- Apatite crystalline phase was formed in the samples with rare-earth content higher than 12 mole (%) total of Rare-earths in the reaction zone.

- 18YSZ, 7DySH and ZrO_2-9.5Y_2O_3-2.2Gd_2O_3-2.1Yb_2O_3 samples have lower reactivity or more resistance to CMAS than the other coating compositions of this work.

Acknowledgements

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